

RELATIONSHIP BETWEEN DENSITY AND COMPOSITION IN MOL PER CENT FOR SOME SOLID SOLUTION SERIES

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ABSTRACT

A general equation relating density to composition in mol per cent is derived for all two component solid solution series wherein volume is an additive property. Dependent upon K , which is defined as the ratio of the molar volume of the end member of higher molecular weight to the molar volume of the remaining component, i.e. $K = V_a/V_b$, the general equation may be graphically represented (density along ordinate) by a concave upward quadratic ($K < 1$), a straight line ($K = 1$), or a convex upward quadratic ($K > 1$). For convenience these three types are labelled type I, II, and III, respectively. Examples of all three types are presented. All ideal solutions should exactly follow one of these types of ideal curves.

Deviation of the empirical data from the theoretical relationship between density and composition is presented as proof for the non-ideality of a solution, since additivity of volume is a necessary property of thermodynamically ideal solutions.

The statistically-fitted curve for the forsterite-fayalite series, previously determined as ideal by the heat of solution measurements of Sahama and Torgeson, proved practically identical to the theoretical curve. The straight line generally used to relate density to composition in mol per cent for this series is definitely erroneous.

INTRODUCTION

A linear relationship between density and mol per cent composition has frequently been assumed in published articles on solid solution series, especially when few data are available. The situation is commonly not so simple; rather a quadratic relationship generally lies closer to the truth. This is particularly true when the molar volumes of the end members differ considerably.

THEORETICAL RELATIONSHIP BETWEEN DENSITY AND COMPOSITION IN MOL PER CENT

If molar volume can be considered as an additive† property in a solid solution series between two components A and B (as it is for an ideal solution: Lewis and Randall, 1923, p. 222) then

$$V = \frac{N_a}{100} V_a + \left(1 - \frac{N_a}{100}\right) V_b \quad (1)$$

where N_a represents the mol per cent of end member A in the mixed crystal, and where V , V_a , and V_b represent the molar volume of the mixed crystal, of pure A , and of pure B , respectively. Gram molecular weight

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† In effect any property which varies linearly with mol per cent composition. For further discussion see any physical chemistry text, for example, that by MacDougall (1943, p. 194).

for this series is undoubtedly an additive property (MacDougall, 1943, p. 194) and therefore

$$M = \frac{N_a}{100} M_a + \left(1 - \frac{N_a}{100}\right) M_b \quad (2)$$

where M , M_a and M_b represent the gram molecular weights of the mixed crystal, of pure A , and of pure B , respectively.

The general relationship between density, ρ , and mol per cent composition, N_a , is theoretically given by division of eq. (2) by eq. (1) thus

$$\rho = \frac{(M_a - M_b)N_a + 100M_b}{(V_a - V_b)N_a + 100V_b} \quad (3)$$

This relationship, in agreement with that developed by Retgers (1889, p. 509), becomes increasingly rigorous as volume approaches additivity for the series.

Where composition is to be calculated from a density measurement, the following form of eq. (3) will be found more convenient:

$$N_a = \frac{100}{1 + K \frac{(\rho_a - \rho)}{(\rho - \rho_b)}} \quad (3a)$$

where

$$K = \frac{V_a}{V_b} = \frac{M_a \rho_b}{\rho_a M_b}$$

and V_a represents the molar volume of the end member with the larger molecular weight. Dependent upon the value of K , eq. (3a) may be graphically represented (density along ordinate) by three types of curves (Table 1).

TABLE 1. THE RELATIONSHIP BETWEEN THE VALUE OF K AND THE TYPE OF THEORETICAL CURVE

Value of K	Type	Description of curve
<1	I	Concave-upward quadratic
1	II	Straight line
>1	III	Convex-upward quadratic

Table 2 presents solutions of eq. (3a) at five selected mixed crystal densities

$$\left(\frac{\rho_a + 3\rho_b}{4}, \frac{\rho_a + 2\rho_b}{3}, \text{ etc.} \right)$$

for 31 solid solution series in which K ranges from 0.85 to 1.15 in steps of 0.01. The utility of Table 2 may be illustrated by considering a hypo-

TABLE 2. COMPOSITION IN MOL. PER CENT, N_a , FOR CRYSTALS OF FIVE INTERMEDIATE DENSITIES BELONGING TO SOLUTION SERIES WITH K VALUES RANGING FROM 0.85 TO 1.15

Value of K^* for the series	Density, ρ , of mixed crystals				
	$\rho_a + 3\rho_b$	$\rho_a + 2\rho_b$	$\rho_a + \rho_b$	$2\rho_a + \rho_b$	$3\rho_a + \rho_b$
	4	3	2	3	4
.85	28.17	37.04	54.05	70.18	77.92
.86	27.93	36.76	53.76	69.93	77.72
.87	27.70	36.50	53.48	69.69	77.52
.88	27.47	36.23	53.19	69.44	77.32
.89	27.25	35.97	52.91	69.20	77.12
.90	27.03	35.71	52.63	68.97	76.92
.91	26.81	35.46	52.36	68.73	76.73
.92	26.60	35.21	52.08	68.49	76.53
.93	26.39	34.97	51.81	68.26	76.34
.94	26.18	34.72	51.55	68.03	76.14
.95	25.97	34.48	51.28	67.80	75.95
.96	25.77	34.25	51.02	67.57	75.76
.97	25.58	34.01	50.76	67.34	75.57
.98	25.38	33.78	50.51	67.11	75.38
.99	25.19	33.56	50.25	66.89	75.19
1.00	25.00	33.33	50.00	66.67	75.00
1.01	24.81	33.11	49.75	66.45	74.81
1.02	24.63	32.89	49.50	66.23	74.62
1.03	24.45	32.68	49.26	66.01	74.44
1.04	24.27	32.47	49.02	65.79	74.26
1.05	24.10	32.26	48.78	65.67	74.07
1.06	23.92	32.05	48.54	65.36	73.89
1.07	23.75	31.85	48.31	65.15	73.71
1.08	23.58	31.65	48.08	64.94	73.53
1.09	23.42	31.45	47.85	64.73	73.35
1.10	23.26	31.25	47.62	64.52	73.17
1.11	23.09	31.06	47.39	64.31	72.99
1.12	22.94	30.86	47.17	64.10	72.82
1.13	22.78	30.67	46.95	63.90	72.64
1.14	22.62	30.49	46.73	63.69	72.46
1.15	22.47	30.30	46.51	63.49	72.30

* K is defined as the ratio of the molar volume of the denser end member, A , to that of the lighter end member, B , i.e. V_a/V_b or $M_a\rho_b/\rho_aM_b$.

thetical solid solution series for which $\rho_a = 2.000$, $\rho_b = 1.000$, and $K = 0.895$. By interpolation from Table 2, five intermediate points (1.250, 27.14%; 1.333, 35.84%; 1.500, 52.77%; 1.667, 69.09%; and 1.750, 77.02%) on the theoretical curve for this series may be quickly secured. These plus the two end points permit an accurate graphical presentation of eq. (3a) for this particular series. The five points also show the deviation of the theoretical curve from linearity (by comparison with the corresponding values for the series where $K = 1$); for example, in this series the deviation from linearity in the $\rho_a + \rho_b/2$ region is +2.77%. The accuracy of the interpolation is high; substituting 2.000, 1.000, 1.500 and 0.895 into eq. (3a) for ρ_a , ρ_b , ρ , and K , respectively, yields 52.77% when the function is solved for N_a .

EXAMPLES

A Series with $K < 1$

Complete solid solution exists between $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. From their respective gram-molecular weights, 394.99 and 360.62, and from the writer's density measurements of 1.9225 and 1.7209, respectively, K can be calculated to be 0.980 for this series. Thus, consulting Tables 1 and 2, one sees that the theoretical curve is concave-upward (Type I) and that it deviates from linearity about 0.51 mol per cent in the 50 mol per cent region.

Crystals of this series were grown from aqueous solutions, their densities measured, then carefully analyzed. Full details of growth, chemical analysis, and density measurements are given by Bloss (1951); results are summarized in Table 3. Densities are believed accurate to ± 0.0005 , composition to within ± 0.5 mol per cent; the empirical values were not rounded off, however, for statistical reasons. The writer's end point values, 1.7209 and 1.9225, which were the results of several determina-

TABLE 3. EMPIRICAL DENSITY-COMPOSITION DATA
FOR THE (Ni, Mg) $(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ series

Mol Per Cent Nickel Member	0.00	21.03	21.20	30.45	42.40	55.46	56.34	65.97	66.18	81.09	81.22	100.00
Density	1.7209	1.7611	1.7626	1.7810	1.8065	1.8304	1.8336	1.8525	1.8543	1.8831	1.8855	1.9225

tions on each of several specimens, agree closely with those in the literature which are for the magnesium member 1.721, 1.7225 (Tutton, 1905, p. 1136), and 1.721 (Perrot's value cited by Tutton, 1905, p. 1136) and for the nickel member 1.9227 (Tutton, 1916, p. 6). From Hofmann's (1931, p. 288) x -ray data, density is calculated to be 1.722 for the

magnesium end member; from Mukherjee's (1935, p. 504) x-ray data, density is calculated to be 2.038 for the nickel end member.

The data of Table 3 were next analyzed statistically. All regressions¹ were carried out in terms of composition upon density (i.e., the lines were calculated which minimized the deviations in composition of the data from them), since the calculated density-composition curves were intended for use in predicting composition from measured density values. Both linear and quadratic equations were fitted to the data by the standard method of least squares (described in Rider, 1939, pp. 27-32); their relative goodness of fit was then compared by means of calculating their *t* value.² This process was performed twice, once double weighting³ the end points and once giving them infinite weight.⁴ Extra weighting of the end points was deemed justifiable since for them composition was known absolutely and, in addition, their density values could be compared with those in the literature. For the assumption of infinitely weighted end points the quadratic

$$g(\rho) = (\rho - 1.7209)(602.76264 - 55.51659\rho) \quad (4)$$

and the straight line

$$f(\rho) = 496.032(\rho - 1.7209) \quad (5)$$

represent the equations of best fit. If the end points are only double weighted, the quadratic

$$h(\rho) = -1028.0653 + 689.6492\rho - 53.5518\rho^2 \quad (6)$$

and the straight line

$$k(\rho) = 494.6053\rho - 850.6854 \quad (7)$$

are the equations of best fit. The functions $g(\rho)$, $f(\rho)$, $h(\rho)$, and $k(\rho)$ represent composition in mol per cent of nickel ammonium sulfate. The proper values for nickel ammonium sulfate and magnesium ammonium sulfate may be substituted into eq. (3a) to get the theoretical relation-

¹ In statistical terminology regression signifies the process of fitting a line to the data which accurately follows their trend yet, at least in part, lacks their chance errors.

² The statistical quantity *t* refers to "Student's" *t* distribution (Mood, 1950, p. 206; Rider, 1939, pp. 88-98). It was here used to compare the linear regression function with the quadratic one developed under similar weighting assumptions; in effect the calculated value of *t* permits a determination of the probability of the data having by chance favored a quadratic distribution even though the relationship investigated was actually linear.

³ Each end member observation was counted twice in making the least square computations.

⁴ Each end member observation was considered to have been made an infinite number of times, mixed crystal observations but once. Under this assumption the statistically derived curves must perforce pass through the end points.

ship for this series, namely,

$$N_{ni} = \frac{100}{1 + K \frac{(\rho_{ni} - \rho)}{(\rho - \rho_{mg})}} \tag{8}$$

where

$$K = \frac{M_{ni}\rho_{mg}}{M_{mg}\rho_{ni}} = 0.98044839.$$

Table 4 indicates the relative accuracies of the various equations in predicting the composition of a mixed crystal from its measured density. Table 5 summarizes the results of statistical tests of the equations and

TABLE 4. COMPARISON OF CURVES RELATING DENSITY TO MOL PER CENT OF NICKEL AMMONIUM SULFATE IN MIXED CRYSTALS OF THE (Mg, Ni)(NH₄)₂(SO₄)₂ · 6H₂O Series

Empirical Results		End Points Given Infinite Weight				End Points Double Weighted				Theoretical Curve	
		Quadratic		Straight Line		Quadratic		Straight Line			
Density	Composition by Analysis	Predicted Composition	Deviation*	Predicted Composition	Deviation*	Predicted Composition	Deviation*	Predicted Composition	Deviation*	Predicted Composition	Deviation*
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1.7209	0.00	0.00	0.00	0.00	0.00	0.16	0.16	0.48	0.48	0.00	0.00
1.7611	21.03	20.30	-0.73	19.94	-1.09	20.39	-0.64	20.36	-0.67	20.25	-0.78
1.7626	21.20	21.05	-0.15	20.68	-0.52	21.13	-0.07	21.10	-0.10	21.01	-0.19
1.7810	30.45	30.28	-0.17	29.81	-0.64	30.33	-0.12	30.21	-0.24	30.22	-0.22
1.8065	42.40	43.01	0.61	42.46	0.06	43.02	0.62	42.82	0.42	42.94	0.54
1.8304	55.46	54.88	-0.58	54.32	-1.14	54.86	-0.60	54.64	-0.82	54.80	-0.66
1.8336	56.34	56.46	0.12	55.90	-0.44	56.43	0.09	56.22	-0.12	56.39	0.05
1.8525	65.97	65.79	-0.18	65.28	-0.69	65.74	-0.23	65.57	-0.40	65.72	-0.25
1.8543	66.18	66.68	0.50	66.17	-0.01	66.62	0.44	66.46	0.28	66.61	0.43
1.8831	81.09	80.80	-0.29	80.46	-0.63	80.72	-0.37	80.71	-0.38	80.76	-0.33
1.8855	81.22	81.99	0.77	81.65	0.43	81.89	0.67	81.90	0.68	81.94	0.72
1.9225	100.00	100.00	0.00	100.00	0.00	99.86	-0.14	100.19	0.19	100.00	0.00

* From empirical data.

TABLE 5. COMPUTED STATISTICAL VALUES FOR EQUATIONS (4)-(8)

Number of Equation in Text	(4)	(5)	(6)	(7)	(8)
Residual Sum of Squares	2.250	4.423	2.169	2.744	2.297
Degrees of Freedom	9	9	9	9	
Value of <i>t</i>	2.948		1.707		
Probability of a Larger Value of <i>t</i> Arising by Chance	0.01		0.10		

indicates that, for the same method of end point weighting, the quadratic function always fitted the data significantly better than did the linear function. Moreover, calculated values of the standard statistical quantity, t , indicate small likelihood that this occurred by chance. Interestingly, the theoretical equation, as judged by its residual sum of squares, fits the data almost equally as well as either of the two statistically fitted quadratics. This statistical analysis leads to the following conclusions for this series:

- (1) the distribution of the empirical data on density and composition in mol per cent is more likely quadratic than linear.
- (2) this distribution coincides almost precisely with that predicted by theoretical eq. (8).

The latter conclusion was further checked. The average density (1.8063 ± 0.0005) and, by chemical analysis, the average composition (42.71 ± 0.5 mol per cent nickel ammonium sulfate) was determined for a group of mixed crystals grown from the same solution. Using the theoretical equation the composition was calculated from the density value to be 42.84 mol per cent.

Series with $K \cong 1$

When the value of K is very close to one, the density—mol per cent composition relationship may be indistinguishably close to linearity. For example, magnesium ammonium chromate, $\text{Mg}(\text{NH}_4)_2(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, and magnesium rubidium chromate, $\text{MgRb}_2(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$, have molar volumes* of 218.3 and 217.4 cc, respectively. Since the rubidium salt has the larger molecular weight, these volumes correspond to V_b and V_a , respectively. Thus for this series K equals 0.996. Tables 1 and 2 indicate that, for this value of K the theoretical curve is an almost linear, very slightly concave-upward quadratic. Table 6 indicates that the empirical data follow the predicted theoretical distribution rather precisely; the densities predicted for the intermediate compositions on the basis of a linear relationship are slightly higher around the 50 mol per cent region than those empirically determined, an indication that the empirical curve is slightly concave upward. Furthermore, Table 2 indicates the deviation from linearity in the 50 mol per cent region to be 0.1 mol per cent or 1 part in 1,000. In terms of density, therefore, this deviation from linearity is -0.0006 . As shown by Table 6, the empirical densities in the 50 mol per cent region, also differ from linearity in the same direction and by approximately the same amount.

* Calculated from Porter's (1925, p. 92) data.

TABLE 6. COMPARISON OF EMPIRICAL DENSITIES OF $(\text{NH}_4, \text{Rb})_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ MIXED CRYSTALS WITH THOSE CALCULATED ON BASIS OF A STRAIGHT LINE THROUGH THE END POINTS

Empirical Data ^a		Intermediate densities calculated from end values on basis of linearity
Mol % Ammonium Magnesium Chromate ^b	Density	
0	2.463	
4.1273	2.437	2.437
14.1170	2.374	2.374
23.8121	2.313	2.313
35.2616	2.241	2.242—
45.9248	2.174	2.175—
54.1927	2.122	2.123—
60.8866	2.080	2.081—
73.9891	1.998	1.998
84.4436	1.932	1.933—
94.5609	1.869	1.869
100.0000	1.835	

^a Porter (1925, p. 92).

^b Recalculated from weight per cent by the writer. The third and fourth decimal places were retained for computational purposes only.

A Series Where $K > 1$

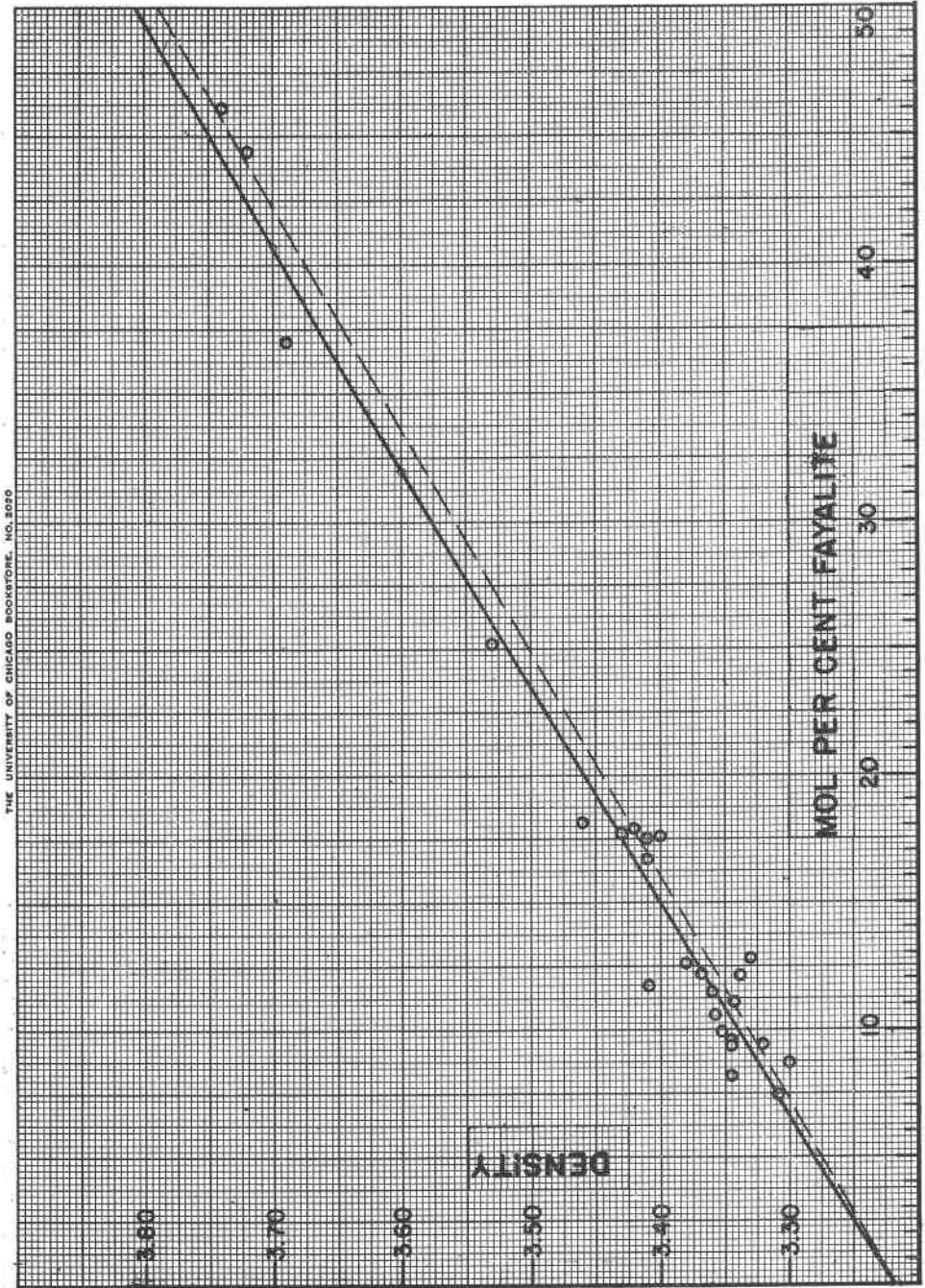
An example of this type is the forsterite-fayalite solid solution series. Unfortunately, reported densities for forsterite range from 3.19 to 3.22, those for fayalite from 4.07 to 4.34, the low determinations being generally derived from artificial crystals. The data of Table 7, collected from the literature, were therefore restricted to fairly recent determinations on natural crystals.

A quadratic equation was fitted to the data by the method of least squares; the curve which best fit the data (minimized the sum of the squares of the deviations of the empirical points from it) was determined to be,

$$q(\rho) = -207.754 + 47.68521\rho + 5.25529\rho^2 \quad (9)$$

where $q(\rho)$ represents mol per cent fayalite as a function of the density, ρ , of mixed crystals of the forsterite-fayalite series.

Solution of the equation for ρ , when $q(\rho)$ is set equal to 0.00 and 100.00 mol per cent, respectively, yields the density values 3.217 ± 0.005 for forsterite and 4.36 ± 0.01 for fayalite. These values, in effect based upon the work of several investigators on 30 crystals of differing fayalite content, are assumed to be the most reliable available although they



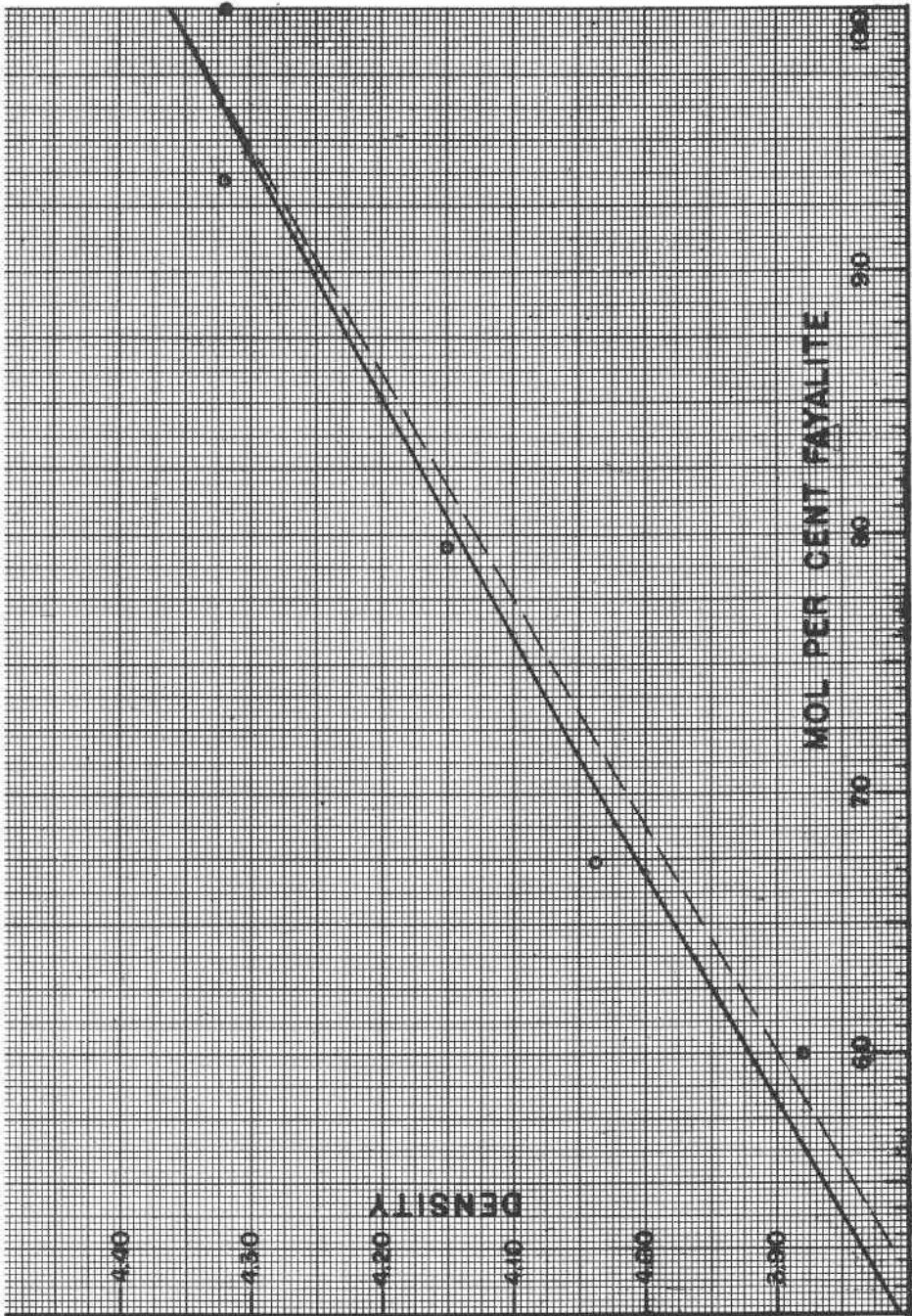


FIG. 1. The relationship between density and composition for natural crystals of the forsterite-fayalite series. The open circles represent the data of Table 7. The solid line curve indicates both the statistically derived quadratic of best fit as well as the theoretical equation secured by substituting the fitted quadratic's end points into the general theoretical equation. Only 37% of the assembled mixed crystal data plot below the dashed straight line joining the quadratic's end points; if the fayalite end point is assumed to represent a density of less than 4.36, this discrepancy from a linear distribution becomes even greater.

TABLE 7. COLLECTED DENSITY DATA ON NATURAL CRYSTALS OF THE FORSTERITE-FAYALITE SERIES

Mol % Fayalite ^a	Sp. G.	Source
7.4	3.309	Sandell and Goldich (1943, p. 177)
8.2	3.346	Gossner (1929, p. 177)
8.7	3.30	Hawkes (1946, p. 281)
9.3	3.347	Lauro (1940) [M.A. 10, p. 420]
9.4	3.321	Sandell and Goldich (1943, p. 177)
9.6	3.345	Sahama and Torgeson (1949, p. 3-5)
9.9	3.353	Sahama and Torgeson (1949, p. 3-5)
10.6	3.357	Gossner (1929, p. 177)
11.1	3.343	Ernst (1925, p. 138-9)
11.4	3.360	Aurousseau and Merwin (1928, p. 560)
11.7	3.409	Gossner, (1929, p. 177)
12.1	3.338	Sahama and Torgeson (1949, p. 3-5)
12.2	3.369	Aurousseau and Merwin (1928, p. 560)
12.6	3.38	Aurousseau and Merwin (1928, p. 560)
12.8	3.33	Mathias (1949, p. 488)
16.7	3.410	Carobbi (1928) [M.A. 4, p. 138]
17.5	3.41	Spencer (1932, p. 40)
17.6	3.40	Harada (1936, p. 294)
17.7	3.43	Esenwein (1929, p. 126)
17.9	3.42	Harada (1936, p. 294)
18.1	3.462	Carobbi (1928) [M.A. 4, p. 138]
25.2	3.53	Mathias (1949, p. 489)
37.0	3.69	Deer and Wager (1939, p. 19-20)
44.4	3.72	Sahama and Torgeson (1943, p. 5-6)
46.1	3.74	Sahama and Torgeson (1949, p. 5-7)
60.0	3.88	Deer and Wager (1939, p. 19-20)
67.4	4.038	Penfield and Forbes (1896, p. 131-2)
79.5	4.15	Deer and Wager (1939, p. 19-20)
93.5	4.32	Palmgren (1916, p. 117)
100.0	4.318	Penfield and Forbes (1896, p. 130)

^a Since the density of tephroite is very close to that of fayalite, mol per cent tephroite was included as mol per cent fayalite.

vary somewhat from those generally cited in the literature (Table 8).

K for this series is calculated from the newly calculated density values to be approximately 1.069. On this basis the theoretical relationship between mol per cent fayalite, N_{fa} , and density, ρ , is for the series

TABLE 8. DENSITY VALUES OF OLIVINE END MEMBERS CITED IN LITERATURE

Substance	Density	Source
Forsterite (artificial)	3.223	Aurousseau and Merwin, (1928, p. 563)
Forsterite (artificial)	3.216	Bowen and Anderson, (1914, p. 498)
Forsterite (pure)	3.19	Handbook of Physical Constants, (1942, p. 10)
Fayalite (pure)	4.14	Handbook of Physical Constants, (1942, p. 10)
Fayalite (artificial)	4.068	Handbook of Physical Constants, (1942, p. 15)
Fayalite (natural)	4.318	Penfield and Forbes (1896, p. 130)

$$N_{fa} = \frac{100}{1 + 1.0685366 \left(\frac{4.36 - \rho}{\rho - 3.217} \right)} \quad (10)$$

which is graphically represented by a convex upward curve.

In Table 9 compositions predicted from density by the fitted quadratic eq. (9) are compared with those predicted by theoretical eq. (10). Since the end member densities used in the theoretical equation were derived from the fitted quadratic, the close agreement of the two near the end compositions was anticipated. Their exceedingly close agreement for intermediate compositions, however, strongly suggests that the forsterite-

TABLE 9. FORSTERITE-FAYALITE SERIES. COMPOSITIONS PREDICTED BY SUBSTITUTING DENSITY VALUES INTO THE STATISTICALLY FITTED EMPIRICAL QUADRATIC EQUATION AND INTO THE THEORETICAL EQUATION

Density	Predicted Composition (in Mol Per Cent Fayalite)	
	By Fitted Quadratic	By Theoretical Equation
3.217	0	0
3.300	6.84	6.83
3.400	15.13	15.14
3.500	23.52	23.55
3.600	32.02	32.05
3.700	40.63	40.65
3.800	49.34	49.35
3.900	58.15	58.15
4.000	67.07	67.06
4.100	76.10	76.07
4.200	85.23	85.18
4.300	94.46	94.41
4.360	100.00	100.00

fayalite data closely adhere to the theoretical curve and are not linearly distributed as commonly assumed. Figure 1 shows a plot of the collected data, of the theoretical curve (for all purposes identical to the fitted quadratic), and of the commonly accepted straight line joining the end points.

Further corroboration of the close adherence of the forsterite-fayalite density-composition data to the theoretical curve may be derived from thermodynamic considerations. Since volume is necessarily an additive property for all ideal solutions (Lewis and Randall, 1923, p. 222) and since deviations from the theoretical equation can be expected only when volume is not additive, theoretical eq. (3) should be valid for all ideal solid solutions. In particular, since the heat of solution measurements of Sahama and Torgeson (1949) established the forsterite-fayalite series as a thermodynamically ideal solid solution, the density-composition relationships for this series should therefore follow the theoretical equation.

Where the density-composition relationships do not follow theoretical equation (3), even in the face of accurate data on the density and molecular weight of the end points, the solid solution being investigated may be assumed to be non-ideal.

CONCLUSIONS

1. For all ideal solid solution series the following equation accurately expresses the relationship between density, ρ , and composition for mixed crystals of the series:

$$\rho = \frac{(M_a - M_b)N_a + 100M_b}{(V_a - V_b)N_a + 100V_b} \quad (3)$$

where N , M , and V refer by subscript to mol per cent, gram-molecular weight, and molar volume, respectively, of the two end members, A and B . The equation is numbered as in the text.

2. Solution of eq. (3) for N_a , the mol per cent of A in the mixed crystal, yields the more useful equation:

$$N_a = \frac{100}{1 + K \left(\frac{\rho_a - \rho}{\rho - \rho_b} \right)} \quad (3a)$$

where

$$K = \frac{V_a}{V_b} = \frac{M_a \rho_b}{\rho_a M_b};$$

and where substance A , by definition, has the larger molecular weight.

Thus, if the densities and molecular weights of the end members are known, the composition of an ideal mixed crystal may be calculated from its measured density.

3. Both equations are non-linear in general; only in the special case where $K=1$ do they become linear.

4. Graphically expressed with density along the ordinate, the theoretical relationship follows one of three types of curves dependent on the value of K for the series. (See Table 1 of text.)

5. The relationship between density and composition for non-ideal solutions will follow the theoretical relationship only to the extent that their molar volumes approach additivity. However, non-additivity of volume can hardly be expected to produce a relationship between density and composition more simple than that expressed by eqs. (3) or (3a).

6. Consequently, linear relationships between density and composition, especially where refined measurements are made, should be relatively rare. Statistically fitting a quadratic equation to the data is to be preferred over the practice of ruling a straight line through the plotted points. Where the data are too meager for statistical analysis, the theoretical equation should give better results than such a straight line, even for non-ideal solutions.

7. Where the densities are known only for analyzed crystals of intermediate compositions, the densities of the end members may be secured by either of two ways: (1) statistically fitting a quadratic to the density-composition data and solving it for the densities at 0 and 100 mol per cent compositions (as was done for the olivines in this paper), or (2) computing the molar volumes for the intermediate members and statistically fitting a linear equation to the data with subsequent solution of this equation to yield the molar volume of the end members (from which the densities may be calculated).

8. Deviation of empirical density-composition data from the theoretical relationship of eq. (3) or (3a) indicates the solution to be a non-ideal one.

9. The following solid-solutional series adhere to the theoretical relationship between density and composition:

- (a) $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Type I curve)
- (b) $\text{Mg}(\text{NH}_4)_2(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{MgRb}_2(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Type II curve)
- (c) Forsterite-fayalite (Type III curve)

10. Of particular interest, the forsterite-fayalite curve relating density to mol per cent is not linear as commonly assumed.

11. The density of pure natural forsterite is computed to be 3.217 ± 0.005 ; that of pure natural fayalite, 4.36 ± 0.01 .

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